CHEM 371: Lecture 7

● Illustrative calculation of time correlation functions

1. The isolated harmonic oscillator

(Ref.: Luban and Luscombe, Am. J. Phys. **67**, *1161* (1999))

The problem we're now going to consider as an illustration of some of the ideas we've developed in the earlier lectures is somewhat artificial. It is the problem of finding a TCF – in this case, specifically the position autocorrelation function – of a single one-dimensional harmonic oscillator at the temperature *T*. The artificiality of the model lies in the fact that we're going to treat the oscillator as an isolated system and yet imagine that it is in thermal contact with a heat bath. The bath is necessary to impart a given temperature to the oscillator, but in the absence of interactions there's no mechanism by which energy can be exchanged between the system and its surroundings. So there's an inconsistency in asserting that the oscillator is both isolated and at the temperature *T*. Nevertheless it's worthwhile to study the model so as to get a feeling for how the principles of time-dependent statistical mechanics are actually applied in practice.

Our goal will be to calculate the quantity $\langle x | x(t) \rangle$, where $x(t)$ is the displacement of the oscillator from some origin at time t, and $x \equiv x(0)$. From the definition of ensemble averages,

$$\langle x | x(t) \rangle = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp f_0(x, p)\, x\, x(t; x, p) \tag{1}$$

To evaluate the right-hand side, we need expressions for $f_0(x, p)$ and $x(t; x, p)$. For a system in equilibrium at the fixed temperature *T*, the density distribution f_0 is just the Boltzmann distribution, $f_0 = Q^{-1} \exp(-\beta H)$, where Q is the canonical partition function (defined as $Q = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \exp(-\beta H)$) and H is the system's Hamiltonian. (Factors of Planck's constant in the definition of f_0 and Q can be omitted since they eventually cancel.) The Hamiltonian of the system (the sum of kinetic and potential energies) is given by

$$H = \frac{1}{2m} p^2 + \frac{1}{2} k x^2 \tag{2}$$

Since the oscillator has been assumed to be isolated, it evolves in time according to the equations

$$\dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m}, \qquad \text{and} \qquad \dot{p} = -\frac{\partial H}{\partial x} = -kx \tag{3}$$

These equations can be combined into a single equation for the evolution of x:

$$\ddot{x} = -\frac{k}{m}x, \tag{4}$$

which is easy to solve; the solution will contain two constants of integration, $x(0) \equiv x$ and $p(0) \equiv p$, and when it is substituted into (1), the integrals over x and p can be carried out, and $\langle x | x(t) \rangle$ thereby determined.

A convenient way of solving (4) is by the method of Laplace transforms (which we'll introduce later, in a different calculation), but now we'll take an alternative tack, using instead an approach based on the Liouville operator L. From its definition, this operator is seen to be

$$iL = \dot{x}\frac{\partial}{\partial x} + \dot{p}\frac{\partial}{\partial p}$$

$$= \frac{p}{m}\frac{\partial}{\partial x} - kx\frac{\partial}{\partial p} \tag{5}$$

Formally, $x(t)$ is now given by the expression $x(t) = e^{itL}x$, which, using the series representation of the exponential, leads to

$$x(t) = \left[1 + t\left(\frac{p}{m}\frac{\partial}{\partial x} - kx\frac{\partial}{\partial p}\right) + \frac{t^2}{2!}\left(\frac{p}{m}\frac{\partial}{\partial x} - kx\frac{\partial}{\partial p}\right)\left(\frac{p}{m}\frac{\partial}{\partial x} - kx\frac{\partial}{\partial p}\right) + \right.$$

$$\left. + \frac{t^3}{3!}\left(\frac{p}{m}\frac{\partial}{\partial x} - kx\frac{\partial}{\partial p}\right)\left(\frac{p}{m}\frac{\partial}{\partial x} - kx\frac{\partial}{\partial p}\right)\left(\frac{p}{m}\frac{\partial}{\partial x} - kx\frac{\partial}{\partial p}\right) + \cdots\right]x$$

$$= x + t\frac{p}{m} - \frac{t^2}{2!}\frac{kx}{m} - \frac{t^3}{3!}\frac{pk}{m^2} + \frac{t^4}{4!}\frac{k^2x}{m^2} + \frac{t^5}{5!}\frac{pk^2}{m^3} - \frac{t^6}{6!}\frac{k^3x}{m^3} + \cdots$$

$$= x\left(1 - \frac{(t\sqrt{k/m})^2}{2!} + \frac{(t\sqrt{k/m})^4}{4!} - \frac{(t\sqrt{k/m})^6}{6!} + \cdots\right) +$$

$$+ \frac{p}{m}\sqrt{\frac{m}{k}}\left(t\sqrt{k/m} - \frac{(t\sqrt{k/m})^3}{3!} + \frac{(t\sqrt{k/m})^5}{5!} - \cdots\right) \tag{6}$$

Denoting the factor $\sqrt{k/m}$ as ω, and resumming the series, we find that (6) reduces to

$$x(t) = x\cos\omega t + \frac{p}{m\omega}\sin\omega t \tag{7}$$

which is the sought-for solution for $x(t)$; it can be shown to agree with the solution obtained by the more conventional Laplace transform method. In the above expression, *x* and *p* are the initial values of position and momentum, and correspond to two unknown constants of integration.

After substituting the expressions for *x*(*t*) (from (7)) and f_0 into (1), we get

$$\langle x \,|\, x(t)\rangle = \frac{1}{Q}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp\, x\left(x\cos\omega t + \frac{p}{m\omega}\sin\omega t\right)\exp\left(-\frac{\beta k x^2}{2} - \frac{\beta p^2}{2m}\right)$$

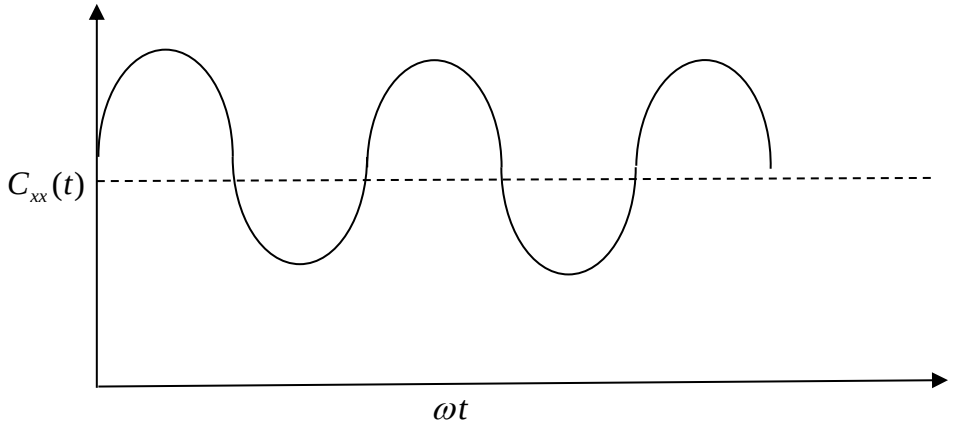
$$= \frac{\cos\omega t}{Q}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp\, x^2 \exp\left(-\frac{\beta k x^2}{2} - \frac{\beta p^2}{2m}\right)$$

$$= \frac{k_B T}{k}\cos\omega t$$

So finally,

$$C_{xx}(t) = \langle x \,|\, x(t)\rangle = \frac{k_B T}{m\omega^2}\cos\omega t \tag{8}$$

A plot of this TCF as a function of the dimensionless time ωt looks schematically like this:

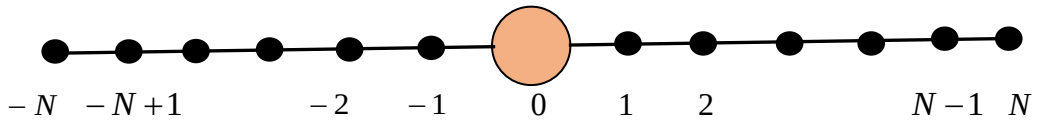


This oscillatory behavior, which persists indefinitely, is not in line with physical intuition for the following reasons: at very short times, the value of x at time t will not be very different from its value at time 0, and so the product of x and $x(t)$ will be positive. The average of this product over many repeated measurements will therefore also be positive. But at very long times, when $x(t)$ is no longer correlated with $x(0)$, the product $x\,x(t)$ is as likely to be positive as it is to be negative, so that when it is averaged over many measurements, the result will be 0. In other words, as $t \to \infty$, we expect $\langle x | x(t) \rangle \to 0$. The failure of the present model to predict a long-time decay to 0 of $\langle x | x(t) \rangle$ is a reflection of the lack of interactions between the oscillator and its surroundings.

2. An interacting particle model

(Ref.: Zwanzig, *Nonequilibrium Statistical Mechanics*, Sec. 1.7)

In this model, the system of interest is a single heavy particle of mass M that is linked harmonically to a one-dimensional lattice of much lighter coupled harmonic oscillators, each of mass m, (thus, $m << M$), as in the figure below:



The model can be regarded as a highly heuristic representation of a colloid in a thermal environment, the heavy particle corresponding to the colloid, and the lighter particles to a fluid environment. Unlike the model of the oscillator that we'd considered previously, this model includes interactions, and we hope their presence will lead to a more physically sensible picture of the heavy particle's long time dynamics.

There are a total of $2N+1$ particles in the model, and we'll denote their positions and velocities as x_j and v_j, respectively, with j varying from $-N$ to $+N$. We'll also assume that the springs connecting the oscillators all have the same spring constant b. The question we'd like to address is: What is the structure of the velocity autocorrelation function of the heavy particle?

To answer this question we proceed as follows:

First, we write down the Lagrangian of this system. It is given by the expression

$$L = \frac{M}{2}\dot{x}_0^2 + \frac{m}{2}\sum_{\substack{j=-N \\ j\neq 0}}^{N}\dot{x}_j^2 - \frac{b}{2}\sum_{j=-N}^{N-1}(x_j - x_{j+1})^2 \tag{9}$$

The dynamics of the particles are determined by the Euler-Lagrange equations:

$$\frac{\partial L}{\partial x_i} - \frac{d}{dt}\frac{\partial L}{\partial \dot{x}_i} = 0, \qquad i = -N, \ldots., 0, \ldots, N \tag{10}$$

Consider the case of the heavy particle (corresponding to $i = 0$); from (10), its equation of motion is

$$M\ddot{x}_0 = -\frac{b}{2}2(x_{-1} - x_0)(-1) - \frac{b}{2}2(x_0 - x_1)$$

$$= b(x_{-1} - 2x_0 + x_1) \tag{11}$$

For the *i*th particle ($i \neq 0$),

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}_i} = m\ddot{x}_i, \quad i = -N \text{ to } N,\ i \neq 0,$$

while

$$\frac{\partial L}{\partial x_i} = -\frac{b}{2}\sum_{j=-N}^{N-1}\frac{\partial}{\partial x_i}(x_j^2 - 2x_j x_{j+1} + x_{j+1}^2)$$

$$= -\frac{b}{2}\sum_{j=-N}^{N-1}(2x_j\delta_{i,j} - 2x_j\delta_{i,j+1`} - 2x_{j+1}\delta_{i,j} + 2x_{j+1}\delta_{i,j+1})$$

$$= -\frac{b}{2}(2x_i - 2x_{i-1} - 2x_{i+1} + 2x_i)$$

$$= b(x_{i-1} - 2x_i + x_{i+1})$$

Thus, the equation of motion of this particle is

$$m\ddot{x}_i = b(x_{i-1} - 2x_i + x_{i+1}) \tag{12}$$

This has the same general structure as the equation for the heavy particle (Eq. (11)), and the two can be written as a single equation by using a Kronecker delta; this equation is

$$[m + (M - m)\delta_{i,0}]\ddot{x}_i(t) = b[x_{i-1}(t) - 2x_i(t) + x_{i+1}(t)] \tag{13}$$

where the time dependence of the positions is shown explicitly.

Although Eq. (13) has the form of a single equation, it actually represents a set of coupled equations, because in order to determine the solution of the equation for the heavy particle, it's necessary to know how the lighter particles labelled -1 and $+1$ evolve in time; their motion, in turn, is governed by the dynamics of their near neighbours, and so on for all the particles in the lattice. This situation is reminiscent of the situation we encountered in the Debye model of solids, where each atom in the solid was coupled to its neighbouring atoms. The way we dealt with the problem there was to introduce a set of so-called normal modes, which decoupled the motions of individual atoms from each other. We'll apply the same idea here.

Specifically, what we do is the following: in place of the coordinates x_i, we now substitute a new collective coordinate q_i, which we define through the relation

$$x_k = \frac{1}{\sqrt{2N+1}} \sum_{j=-N}^{N} q_j \exp[-2\pi ijk/(2N+1)], \qquad k = -N, \ldots, 0, \ldots, N \tag{14}$$

Note that *i* in this expression now stands for $\sqrt{-1}$; it does not represent a particle label. How this transformation allows Eq. (13) to be solved will be discussed in the next lecture.